Surface Plasmon Satellites in 2p X-Ray Satellite Spectra of Transition Metal Halides

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Abstract

The origin of high energy $2P_{1/2}$ and $2P_{3/2}$ x-ray satellites of titanium, copper and Nickel dihalides has been explained using plasmon theory with a new approach by considering both extrinsic and intrinsic contribution simultaneously. Our calculation shows that satellites are due to surface plasmon excitation. We also review the existing calculations and experimental measurements.

Keywords

X-ray satellite spectra; Plasmon; energy separation; Relative intensity; Intrinsic and extrinsic effects.

Introduction

The phenomenon of surface plasmon has been known for a long time. The underlying principles and theories are well understood and a number of publications can be found which discuss their properties in detail. The concept of surface plasmon was first introduced by Ritchie [1] shortly after the discovery of bulk plasmon. In 1957, Ritchie published a series of papers on electron energy losses in thin films, in which he described that plasmon, can also exist near the surface of metals and thus Ritchie represented first theoretical description of the surface plasmon. Gabor [2] attempted to develop the theory to describe the energy loss characteristics of electrons passing through finite metal crystals. As Ritchie [1] pointed out,

Gabor mistakenly assumed electric field is always zero at the surface of the crystal, which led to unrealistic results. Rithcie [1] corrected this and applied more realistic boundary conditions to calculate the electron interactions in extremely thin films. His work resulted in the prediction of surface plasmons and consequently pioneered a whole new field of interest in surface physics. However, in Maxwell's theory it has been already shown that electromagnetic surface waves can also propagate along a metal surface or a metal film with a broad spectrum of eigen frequencies. Using this idea Ritchie theoretically proved that surface plasmon simply arise as purely 2D solutions of Maxwell's equations that propagate as transverse magnetic wave along the metallo- dielectric interface and hence, calculated surface plasmon energy as- $\hbar\omega_s = \hbar\omega_p/\sqrt{2}$; where ω_p = bulk plasmon frequency. This equation is valid for free electron model, but to a fairly good approximation. It can also be used for semiconductors and insulators. Ritchie's [1] prediction of surface plasmon was confirmed in a series of experiments carried out by Powell and Swan [3] who demonstrated the existence of collective electronic oscillations at the surface of Mg and Al. Shortly after, Stern and Ferrell [4] pointed out that surface electromagnetic waves at a metallic surface involve electromagnetic radiation coupled to the surface plasmon. They showed that surface plasma frequency not only depend upon bulk plasmon frequency, but also depends upon dielectric constant of second medium (ε_2) adjacent to the metal. This is due to fact that a part of restoring field of surface plasma oscillation also extends beyond the metallic boundary. Thus the surface plasmon frequency is given by equation-

$$\omega_s = \omega_p/\sqrt{(1+\varepsilon_2)}$$

For a complete clear metal surface in a vacuum $\varepsilon_2 = 1$, and so above equation reduces to Ritchie equation [1]. Since then there has been significant advance in both theoretical and experimental investigations of collective modes in the vacuum solid interface. The renewed interest of surface plasmon has come from x-ray satellite spectra in transition metal halides. In a particular case, the collective excitation of electrons in the bulk of transition metal halides has been extensively discussed, while the surface plasmon excitation has been less frequently studied. In this paper we focus exclusively on surface plasmon excitation in of titanium and copper and nickel halides.

X-ray satellites or non-diagram on high energy side of parent emission lines are well known in x-ray emission spectra. Plasmon theory has been used very successfully in explaining the origin of all those high energy satellites which are found at an energy

separation of ħω$_p$ (plasmon energy) from the main emission x-ray line. This theory has been also used in explaining many α, β and γ satellites [5-7]. The involvement of plasma oscillation in X-ray emission spectroscopy (XPS) data have been studied by many authors and their origin has been the source of active debate for a ling time. Among them satellite structure in halides have received much attention [8-14] and have been the subject of controversy for some time. Several workers [5-6, 15] have explained various satellites in halides using plasma oscillation theory, but could not provide a satisfactory result in calculation of relative intensity. In the present paper we have applied a new approach for explaining the origin of 2P$_{1/2}$ and 2P$_{3/2}$ satellites in titanium and copper and nickel halides using plasmon theory in the new light. The experimental data for titanium compounds were taken form ref. [16-18]; for copper halides from reference [19] and for nickel halides [20].

The collective oscillation experienced by electron density of solid due to certain charge imbalance is called plasma oscillation [21-22]. Pine defined the energy of these collective oscillations as plasmon [23]. In X-ray photoemission process the transiting valance electron excites a plasmon in valance band. The transition energy of main line is thus shared between plasmon (ħω$_p$) and the emitted photon is of low energy. However, if the plasmon pre-exists, then during x-ray photoemission process it can transfer its energy (ħω$_p$) to the transiting valance electron before it annihilates the core vacancy. Thus energy of emitted x-ray photon will be higher than the energy of main line by amount (ħω$_p$). The emission line owing to this process is known as high energy satellites (HES) and has been observed by large number of workers [24-27]. According to what has been said above, the energy separation of energy satellite from main emission line should be equal to plasmon energy, which can be calculated by the formula given by Marton et. al. [28].

Table1: Energy Separation of Compounds (eV)

Compounds	Z'	σ	W		Calculated energy separation		Observed energy	
				$\hbar\omega_p$	$\hbar\omega_s$	$2\hbar\omega_s$	Separation[16-20]	
2P$_{1/2}$satellites								
TiCl$_4$	6	1.73	189.73		4.76		4.0	
						9.5	9.7	
TiO$_2$	8	4.23	79.87		13.3		13.3	
CuF$_2$	3	4.23	101.54		7.2		7.0	[19]
CuCl$_2$	3	3.39	134.44	7.9			8.8	[19]
CuBr$_2$	3	4.71	223.31			10.0	10.0	[19]
2P$_{3/2}$satellites								
NiF$_2$	2	4.72	96.71		6.4		5.5	[20]
NiCl$_2$	3	3.55	129.62		5.8		5.5	[20]
NiBr$_2$	3	5.10	218.53		5.4		5.0	[20]
NiI$_2$	3	5.22	312.5		4.6		4.4	[20]

Bulk plasmon energy = 28.8 $(Z'\sigma/W)^{1/2}$ (ev)

Where Z' = effective number of electrons taking part in plasma oscillation, σ = specific gravity, W = molecular weight of compounds. This equation is valid for free electron model, but to a fairly good approximation, it can be used for semiconductors and insulators. Since at the surface more a localized oscillation can occur with frequency ω_s also depending upon conditions and the energy of corresponding peak, surface plasmon may also be seen, we also calculated surface plasmon energy using formula given by Ritchie [1].The present calculated values of surface plasmon energy in Table-1 are in better agreement with experimentally observed [16-20] values.

Table2: Relative Intensity of Compounds

Compounds	r_s	α	Intensity assignment	Relative Intensity Present work	observed relative intensity see ref. [16-20]	
2P$_{1/2}$satellite						
TiCl$_4$	4.6	1.01	$\beta^2/2\alpha$	0.15	0.12[a]	[16]
			$\beta^2/2\alpha + \beta^3/6\alpha^2$	0.18	0.28	
			β-0.1	0.45	0.41[b]	[17]
TiO$_2$	4.6	1.01	$\beta + \beta^2/2\alpha$	0.33	0.40	
CuF$_2$	2.3	0.72	$\beta + \beta^2/2\alpha$	0.52	0.80	[19]
CuCl$_2$	3.5	0.88	$\beta + \beta^2/2\alpha$	0.49	0.60	[19]
CuBr$_2$	3.3	0.98	$\beta - 0.1$	0.43	0.45	[19]
2P$_{3/2}$satellite						
NiF$_2$	3.8	0.92	$\beta - 0.1$	0.36	0.33	[20]
NiCl$_2$	4.0	0.94	β	0.48	0.51	[20]
NiBr$_2$	4.2	0.97	β	0.51	0.48	[20]
NiI$_2$	4.2	1.02	$\beta^2/2\alpha + \beta^3/6\alpha^2$	0.20	0.29	[20]

a) Experimental results form solid state measurement [16]

b) Experimental results form gas phase measurement [17]

Relative intensity calculation

Energy separation alone is sufficient to prove the involvement of surface plasmon in these satellites but in order to further confirm we also calculated the relative intensity (I_s/I_m) using plasmon theory in new light. There are two types of plasmon excitation– intrinsic and extrinsic [29]. A sudden change in potential due to creation of core hole results intrinsic plasmon excitation (slow electron process). On the other hand, extrinsic plasmon excitation results from Coulomb interaction of the conduction electrons with the photoelectron traversing through the solid from the photoemission site to the surface (fast electron process). Besides, an interference effect can also be visualized as the interaction between the localized photo-hole (intrinsic) and the out going photoelectron (extrinsic) in which the virtual plasmon created by one is absorbed by the other. It has been observed that the contributions of both intrinsic and extrinsic plasmon excitations in photoelectron spectrum overlap one another, so that they are not readily separable experimentally. Also the question whether the

photoemission satellites spectra seen are intrinsic or extrinsic in nature has aroused much controversy. Thus in order to analyze the spectrum a more detailed theoretical investigation is needed. Now in the present paper author has tried to incorporate both the processes i.e. the relative contribution of extrinsic process as well as the second intrinsic process. Pardee et. al. [30] have done the remarkable job in combining both extrinsic and intrinsic effects in one equation simultaneously with some inelastic effects and have given formula for the combined relative intensity as-

$$i = \alpha^n \sum\nolimits_{m=0}^{n} \frac{\left(\beta/\alpha\right)^m}{m!} \tag{2}$$

$$\text{where } \alpha = (1 + l/L)^{-1} \tag{3}$$

is inelastic loss factor, which gives the relative intensity for extrinsic satellite. Here l = mean free path for extrinsic plasmon excitation, L = mean attenuation length for electrons due to processes other than plasmon excitation.

The parameter β is a measure for the probability $P_i(n)$ for intrinsic excitation of n plasmons

$$P_i(n) = e^{-\beta} \; (\beta^n / n!) \tag{4}$$

The value of β [31-34] is taken as $\beta = 0.12 r_s$ \tag{5}

which has been used for intrinsic relative intensity by K.S. Srivastava et.al. [5] and clearly an approximation and one of the term of equation (2).

But in the present case Pardee's equation (2) directly with the same values of α and β given by equations (3) and (4) respectively could not be used because it does not give satisfactory results, so it need some modification.

Therefore in the way of modification we for the first time, modified α. We have replaced α from inelastic loss factor to the ratio of cut- of wave vector K_c to the Fermi wave vector as $\alpha = K_c / K_F$ and its value is taken [35] as-

$$\alpha = 0.47 \, r_s^{1/2} \tag{6}$$

Here r_s is dimensionless parameter and is same as used in equation (5); given by [22] as-

$$r_s = (47.11 / \hbar\omega_p)^{2/3} \tag{7}$$

for volume plasmon and for surface plasmon $r_s = (47.11 / \hbar\omega_s)^{2/3}$ \tag{8}

Using this new value of α (eqn.-6) along with β (eqn.-5) in equation, we have calculated a number of excellent results [36-40].

The beauty of equation (2) is that it contains a series of terms, which include both extrinsic and intrinsic contributions along with their relative coupling terms. The first term is purely extrinsic, while second term is purely intrinsic. The other terms are containing the relative contributions of both extrinsic and intrinsic. The specialty of this formula is that each term alone or simultaneously [29-30] with other terms is able to give the relative intensity. It is the type of excitation, which decides which and how many terms will be used. This formula also includes both the categories mentioned by Bradshaw [41] and gives better results as compared to that and than traditional methods for calculation of the relative intensity. Using equations (2), (4), (5) and (6) the calculated values of relative intensity are given in table -2 simultaneously with experimentally observed values. Earlier workers [5-7, 15] have used various terms of this formula alone to explain successfully the relative intensity of many satellites up to certain extent. But, by using various terms or their relative combination we are able to calculate not only the relative intensity of existing satellites, but also it is possible to predict those satellites which are yet to be discovered. It is also beauty of the method that the relative intensity of higher order satellites can easily be calculated without going in much mathematical details. It is also possible to separate the relative contributions of extrinsic and intrinsic excitations in total intensity. No method is present in the literature which proves the strength of much higher satellites and separates these contributions with such accuracy.

Conclusion

Authors calculated values of plasmon energies of compounds agree well with the experimentally observed values of energy separation. Now for the calculation of relative intensity compounds are treated microscopically [42-44]. When treated in this way, the satellites of different compounds slightly differ in assignment from one another in natural way as types of halides differ. There is only difference for CuF_2, $CuCl_2$ and NiI_2 showing low intensity. This might be due to any other reason. Our calculation establishes that the satellites of $2p_{1/2}$ main line of $CuCl_2$ due to bulk plasmon excitation while other compounds are due to surface plasmon excitation and the consideration of relative contributions of both extrinsic and intrinsic play an important role in the calculation of relative strength of satellites.

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